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# Simulation of MoS<sub>2</sub> crystal structure and the experimental study of thermal decomposition

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#### 1. Introduction

MoS<sub>2</sub> is the main component of molybdenite which is the raw material to produce molybdenum metal products and chemical products. Molybdenite treatment can be classified into two major categories including hydrometallurgy and pyrometallurgy. The common feature of these two methodologies is the conversion of sulfide ore to oxide and its salts, then the further purification of intermediates and finally the reduction to molybdenum metal [1]. This long process of molybdenum metallurgy will cause SO<sub>2</sub> emission and environmental pollution. Buker and Colo [2] made small balls with fine particles of high-purity MoS<sub>2</sub> concentrate and loading materials with full reaction, further thermal treatment with hydrogen at high temperature under vacuum conditions and purification so that the molybdenum metal with its purity not less than 90% was obtained. The production of molybdenum powder by direct decomposition of molybdenum concentrate has probably become a novel method with short flow, less pollution and low cost. The study of the structure and properties of MoS<sub>2</sub> is very meaningful for the further study on the thermal decomposition of molybdenite. However, it is very difficult to simulate the chemical reaction accurately by experimental method. The relevant chemical reactions can be descript in details and the mechanisms can also be revealed by quantum chemical calculations containing density functional theory (DFT) and molecular entity vacancy model (VEMM), etc. [3-6].

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#### ABSTRACT

In this paper, the theoretical calculations of  $MoS_2$  crystal geometries, energy band structure, electron density, electron density difference, density of states and Mulliken overlap population were carried out by density functional theory (DFT). The dynamics simulations of  $MoS_2$  crystal face (0 0 1) were performed. We obtained the meaningful parameters and explanations to guide the thermal decomposition of  $MoS_2$ . The experimental results of the thermal decomposition of  $MoS_2$  were in accordance with the theoretical calculation results. The production of molybdenum powder by direct decomposition of molybdenum concentrate, as a novel method with short flow, less pollution and low cost, was of guiding significance for the next step of the experimental study of thermal decomposition of  $MoS_2$ .

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Density functional theory (DFT) is based on ab initio method of quantum mechanics, which describes the physical properties of the ground state of the system with particle density. Through decades of study, density functional theory is widely used in physics, chemistry, biology, materials and other disciplines. Spirko et al. [7] calculated the defect structure of 2H–MoS<sub>2</sub> based on density functional theory and compared with the experimental results. In 2000, Sun [8] calculated the relationship between the constructed mechanical activated sulfide ore model and flotation agent with the ab initio method based on DFT level and Accelrys workstation CASTEP package. Based on DFT calculations, Borges et al. [9] studied the possible influence of the microwave absorption on the adsorption of thiophene on MoS<sub>2</sub>.

In this paper, the theoretical calculations of MoS<sub>2</sub> crystal geometries, energy band structure, electron density, electron density difference diagram, projection drawing of density of states and Mulliken overlap population, calculations of the mechanisms of thermal decomposition and dynamics simulation were studied by density functional theory (DFT) [10,11], which plays a guiding role of the thermal decomposition of molybdenite. By the thermal decomposition of MoS<sub>2</sub>, it was confirmed that the theoretical calculations and experimental results were in good agreement.

#### 2. Theoretical calculations and experiment

#### 2.1. Theoretical calculations

Based on the ab initio program of CASTEP quantum mechanics of the pseudo-potential plane-wave method in density functional



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theory (DFT), the calculations of the crystal structure of MoS<sub>2</sub> and molecular dynamics simulation of its thermal decomposition were carried out. The geometric crystal structure, energy band, the density of states and other various properties can be predicted accurately by this program. The generalized gradient approximation-Perdew Burker Ernzerhof (GGA-PBE) [12,13] functional, exchange-correlation functional, were adopted in this calculation, which is better than local density approximation (LDA) [14,15] functional and the preferred method used in the studies of molecular and materials properties currently. Compared with LDA, all the parameters in Perdew Burker Ernzerhof (PBE) are fundamental constants. The exchange part of this function is similar with Becke formula while the correlation part is close to Perdew-Wang function. In addition, this function has a strong physics background and reliable numerical results which are frequently used in DFT calculations. Ultra-soft pseudo-potential was used and the spin-polarization of the system was ignored in the calculation with its plane wave 270 eV cutoff and the thickness of the two adjacent vacuum layers 1 nm. Whether the energy and charge density distribution of the system is based on convergence in the self-consistent process are the criteria, the accuracy of the energy convergence is better than  $2 \times 10^{-5}$  a.u. and the quality *k*-point separation in 0.05 Å<sup>-1</sup>.

 $MoS_2$  belongs to hexagonal crystal system and layered structure (see Fig. 1) [16],  $D_{6h}^4$  crystal system and P63 space group. The lattice constants are a = 0.315 nm, c = 1.230 nm and Z = 2. In the crystal structure, the surface network composed by  $Mo^{4+}$  was sandwiched between the upper and lower surface network formed by the  $S^{2-}$ , which formed a trigonal column coordinated structure layer together. [MoS<sub>6</sub>] formed a trigonal column coordinated polyhedron and this structure layer was composed of and linked with empty octahedral layers.

Therefore, the cutting scheme of the calculation model of the nature of  $MoS_2$  crystal structure were as follows: three layers were chosen along the crystal face (1 0 0) of  $MoS_2$  and then expanded



Fig. 1. The crystal structure of MoS<sub>2</sub>.

Table 1			
The ingredients	of raw	materials	$(MoS_2).$

into a 2 × 1 super cell, to form a surface layer (1 0 0) [abbreviated as (1 0 0) slab]; five layers were chosen along the crystal face (1 1 0) of MoS<sub>2</sub> and then expanded into a 1 × 3 super cell, to form a surface layer (1 1 0) [abbreviated as (1 1 0) slab]; and two layers were chosen along the crystal face (0 0 1) of MoS<sub>2</sub> and then expanded into a 2 × 1 super cell, to form a surface layer (0 0 1) [abbreviated as (0 0 1) slab].

The dynamics simulation calculations of the optimized 4MoS<sub>2</sub> slab and 2Mo<sub>2</sub>S<sub>3</sub> slab were carried out under experimental conditions (1823 K, 100 kPa). It was simulated by NPT system, with the simulation time 1.5 ps and time step size 1.0 fs, total 1500 steps, the 500 steps simulation for equilibration phase in initial stage, and later 1000 steps for the dynamic simulation results. The Nosé thermostat [17] and Andersen barostat [18] was used in the dynamic simulation. The molecular dynamics (MD) simulation in CASTEP is based on the velocity Verlet algorithm for integration of the equation of motion. Molecular dynamics in total-energy DFT schemes is implemented in essentially the same way as in conventional forcefield based methods. The main difference is that the energy and atomic forces are derived by solving DFT equations rather than from empirical potentials of interatomic interactions. Electrons are kept on the Born-Oppenheimer surface by means of explicit electronic structure optimization after each MD step. A side effect of this is that evaluation of force and energy from first principles is always the most computationally expensive part of ab initio MD. As a result, the efficiency of the MD step itself has no impact on the speed of the calculation [19,20].

The calculation model of  $MoS_2$  molecular dynamics Mulliken simulation was obtained as follows: it was cut to a depth of 0.666 along the crystal face (0 0 1) of  $MoS_2$  and then expanded into a 2 × 2 super cell, to form a surface layer (0 0 1) including four Mo atoms and eight S atoms [abbreviated as four  $MoS_2$  slab]. According to the lattice constants of  $MoS_2$ , the  $MoS_2$  unit cell was modeled in CASTEP and was further optimized to form a surface layer (0 0 1) including four Mo atoms and six S atoms [abbreviated as two  $MoS_2$  slab] along the crystal layer (0 0 1). And all the atoms in the studied structures were fully allowed to relax during the optimization procedure.

#### 2.2. Experiment

In order to further validate the thermal decomposition of MoS<sub>2</sub>, the experiment was carried out with MoS<sub>2</sub> (>98.5%) produced by Tianjin Chemical Reagent Factory as raw materials which was listed in Table 1. Differential thermal analysis–thermogravimetry (DTA–TG) curves were obtained by German NETZSCH STA 409 PC/PG simultaneous thermal analyzer, with oxygen as the shielding gas to eliminate the influence of oxygen and flow 30 mL/min, and heating rate 5 K/min.

#### 3. Results and discussion

3.1. Crystal geometries, energy band structure, electron density, electron density difference diagram, projection drawing of density of states and Mulliken overlap population of  $MoS_2$  (1 0 0) slab, (1 1 0) slab and (0 0 1) slab

The periodic density functional theory was adopted to optimize the crystal geometries of  $MoS_2$  (1 0 0) slab, (1 1 0) slab and (0 0 1)

Ingredients	MoS <sub>2</sub>	Fe	SiO <sub>2</sub>	MnO <sub>2</sub>	Acid insoluble materials	Oils
Contents (%)	≥98.5	<0.1	<0.001	<0.2	<0.5	<0.2

slab, and the Mulliken population analysis was also carried out. The calculation results were listed in Table 2.

It was found from Table 2 that the order of the average bond length of Mo–S bond was  $(0\ 0\ 1)$  slab >  $(1\ 0\ 0)$  slab >  $(1\ 1\ 0)$  slab so that the order of the stability was just reversed. So the Mo–S bond in  $(0\ 0\ 1)$  cleavage surface of MoS<sub>2</sub> is the weakest and easiest to break when heated. It was also found that the order of Mulliken overlap population of Mo–S bond in MoS<sub>2</sub> slab was  $(1\ 1\ 0)$ slab >  $(1\ 0\ 0)$  slab >  $(0\ 0\ 1)$  slab, which indicated that the thermal decomposition was easier to take place on  $(0\ 0\ 1)$  cleavage surface.

The electron density and electron density difference diagram of  $MoS_2 (1 \ 0 \ 0)$  slab,  $(1 \ 1 \ 0)$  slab and  $(0 \ 0 \ 1)$  slab were listed in Table 3. It can be seen that the layered structure of  $MoS_2 (0 \ 0 \ 1)$  cleavage caused the close ionic connection in the layer but the interaction force between layers is very weak. So the Mo–S bond in  $MoS_2 (0 \ 0 \ 1)$  cleavage surface is the weakest and easier to be broken than that in other surfaces. This calculation results were in accordance with the dates in Table 2. Therefore, before the treatment of molybdenite mainly composed by  $MoS_2$ , the ores must be crushed along the cleavage surface in order to gain a better effect of the following thermal decomposition. After heated by friction, however, Mo–S bond in  $(0 \ 0 \ 1)$  cleavage surface of  $MoS_2$  which is used as lubricant would easily be broken.

3.2. The theoretical calculation and dynamics simulation of the structure of reactant and product during thermal decomposition of  $MoS_2$ 

The calculation and simulation results were listed in Tables 4–7, respectively. Tables 4 and 5 show the optimized structure,

dynamic simulated structure and bond length of  $4MoS_2$  slab. Tables 6 and 7 show the optimized structure, dynamic simulated structure and bond length of  $2Mo_2S_3$  slab.

The calculation results (Table 4) of the Mulliken bond population of Mo–S bond indicated that the Mulliken bond population of the optimized Mo–S bond was 0.417, but the Mulliken bond population of the simulated Mo–S bond was 0.398, which may attribute to the weakening of bond strength under thermal decomposition.

The calculation results of the energy band and density of state demonstrated that the contribution order of frontier energy band for the optimized structure of  $4MoS_2$  slab was 4d orbit of Mo >3p orbit of S atom and the s orbital contributed less. However, the contribution order of frontier energy band for the dynamic simulated structure of  $4MoS_2$  slab was 3p orbit of S atom >4d orbit of Mo, which was directly related to the further weakening of Mo–S bond strength.

The calculation results (see Table 6) of the average Mulliken bond population of Mo–S bond indicated that the average Mulliken bond population of the optimized Mo–S bond was 0.368, but the average Mulliken bond population of the simulated Mo–S bond was 0.360, which was also related to the further weakening of Mo–S bond strength.

The calculation results (see Table 6) of the energy band and density of state indicated that the contribution order of frontier energy band for the optimized structure of  $2Mo_2S_3$  slab was 4d orbit of Mo >3p orbit of S atom and the s orbital contributed less. However, the contribution order of frontier energy band for the dynamic simulated structure of  $2Mo_2S_3$  slab was 3p orbit of S atom >4d orbit of Mo and the s orbital contributed nothing which was

#### Table 2

The average bond length and Mulliken overlap population of (100) slab, (110) slab, (111) slab, (001) slab of molybdenite.

		MoS <sub>2</sub> (0 0 1)	MoS <sub>2</sub> (100)	MoS <sub>2</sub> (1 1 0)
Bond length (Å)	Mo-S	2.402	2.396	2.389
	Mo-Mo		2.970	2.974
	S–S		1.990	2.976
Bond population	Mo-S	0.38	0.401	0.419
	Mo-Mo		-0.4	-0.69
	S–S		0.5	-0.12
Fermi energy (eV)		4.338	1.721	1.670
Total energy (eV)			-44886.427373	-74811.97513008

#### Table 3

The electron density diagram and electron density difference diagram of (100) slab, (110) slab and (001) slab of molybdenite.

		Electron density diagram	Electron density difference diagram
(100)	$\hat{\mathbf{x}}$		1 🕈 💐 🕯
(110)			
(001)			XXXXXXX
	A A A A A A A A	IN A RACE AND A	

#### Table 4

Optimized structure, dynamics simulated structure of 4MoS<sub>2</sub> slab and theoretical calculation results.



#### Table 5

Bond length of the optimized structure and dynamics simulated structure of 4MoS<sub>2</sub> slab.

Bond length	Mo(8)-S(2)	Mo(8)-S(2')	Mo(5)-S(6')	Mo(5)-S(7')	Mo(3)-S(2')
Opt (Å)	2.405	2.420	2.418	2.418	2.411
Dynamic (Å)	2.588	2.615	2.616	2.639	2.624

directly related to the further weakening of Mo–S bond strength. The calculation results also indicated that compared to  $4MoS_2$  slab, Mo–Mo bond also existed in  $2Mo_2S_3$  slab.

#### 3.3. The mechanisms analysis of thermal decomposition

Some researchers believed that the possible mechanism [21] of the thermal decomposition of MoS<sub>2</sub> under vacuum was as follows:

$$4\text{MoS}_2 \iff 2\text{Mo}_2\text{S}_3 + \text{S}_2 \tag{1}$$

$$2\text{Mo}_2\text{S}_3 \Longleftrightarrow 4\text{Mo} + 3\text{S}_2 \tag{2}$$

They did not think it was the direct decomposition reaction:

$$MoS_2 \iff Mo + S_2$$
 (3)

To further prove the mechanisms (1) and (2) abovementioned, the dynamics simulation calculations of the optimized  $4MoS_2$  slab and  $2Mo_2S_3$  slab were carried out. The calculation results (see Tables 4–7) were in accordance with the mechanism of step-wise thermal decomposition of  $MoS_2$ . Table 5 showed that the average bond length of Mo–S bond was 2.414 Å while the simulated average bond length of Mo–S bond under experimental conditions was 2.484 Å. That meant the bond strength of Mo–S bond weakened after 1.5 ps under experimental conditions but the variations of Mo–S bond in different position was different. By dynamics simulation the bond length of Mo(8)–S(2), Mo(8)–S(2'), Mo(5)–S(6'), Mo(5)–S(7'), Mo(3)–S(2') bond increased. Therefore, S atoms especially S(2) in these positions will be removed first from MoS<sub>2</sub> to Mo<sub>2</sub>S<sub>3</sub> and the further reaction to produce Mo from Mo<sub>2</sub>S<sub>3</sub> during the thermal decomposition.

The reconstruction from  $MoS_2$  to  $Mo_2S_3$  was also studied in the previous literature [22]. It revealed that  $MoS_2$  first transformed to  $Mo_2S_3$  following by the further decomposition during the thermal decomposition. With comparison to the structures and the calculated results of  $MoS_2$  and  $Mo_2S_3$ ,  $MoS_2$  will probably remove S(2')and S(6') first to produce  $Mo_2S_3$ , which was in agreement with the present results in this paper.

#### 3.4. Experimental results of the thermal decomposition of MoS2

DTA-TG curves were shown in Fig. 2 and the XRD patterns of the residues were given in Fig. 3. From XRD patterns it was seen clearly that the main product was Molybdenum metal.

The calculated total energy of optimized structure of 4MoS<sub>2</sub> slab was –9981.206227355 eV and the total energy of the geometric structure by dynamics simulation under experimental conditions

#### Table 6

Optimized structure, dynamics simulated structure of 2Mo<sub>2</sub>S<sub>3</sub> slab and theoretical calculation results.



#### Table 7

Bond length of the optimized structure and dynamics simulated structure of 2Mo<sub>2</sub>S<sub>3</sub> slab.

Bond length	Mo(2)-S(6)	Mo(3)-S(8)	Mo(4)-S(8)
Opt (Å)	2.262	2.474	2.655
Dynamic (Å)	2.646	3.680	5.987

of thermal decomposition was -9978.697270370 eV (see Table 5). It can be seen clearly that the geometric structure by dynamics simulation is not stable and tends to remove part of S atoms to produce Mo<sub>2</sub>S<sub>3</sub>. It was in accordance with the results from Fig. 2 that thermal decomposition of MoS<sub>2</sub> mainly carried out above 1203 °C. The main product of thermal decomposition was Mo<sub>2</sub>S<sub>3</sub> below 1203 °C so that the weight decreased slightly (9.2%) because only part of S atoms were removed. According to the reaction (1), the weight of S<sub>2</sub> produced by complete reaction occupied 10.02% of the total weight of raw materials. These experimental results were in accordance with the theoretical analysis and reaction mechanisms if the purity of raw materials was neglected.

The calculated total energy of optimized structure of  $2Mo_2S_3$  slab was -9418.756090577 eV and the total energy of the

geometric structure by dynamics simulation under experimental conditions of thermal decomposition was -9418.757603823 eV (see Table 6). It can be seen clearly that the geometric structure of  $2Mo_2S_3$  by dynamics simulation is not stable and tends to be stable with the weakening bond strength of Mo–S bond under thermal decomposition conditions, which also contributed to the reason why the thermal decomposition temperature of  $Mo_2S_3$  must be higher than 1203 °C under experimental conditions.

The calculation results were also in agreement with the experimental results of the thermal decomposition of  $MoS_2$ , i.e. desulfuration reaction of thermal decomposition of  $MoS_2$  was carried out above 1203 °C. When the temperature was higher than 1203 °C, in the first step  $MoS_2$  decomposed into  $Mo_2S_3$  which was not stable and would remove the three residual sulfur atoms in the following two steps. Two sulfur atoms were removed first and the other sulfur atom was then removed until molybdenum metal was produced after complete reaction, which was shown in Fig. 3.

#### 4. Conclusions

Based on the pseudo-potential plane-wave method in density functional theory (DFT) and the thermal decomposition



Fig. 2. TG-DTA curve of the thermal decomposition of MoS<sub>2</sub>.



Fig. 3. XRD pattern of the reaction product.

experiment of  $MoS_2$ , mechanics calculation of thermal decomposition of  $MoS_2$  crystal, the dynamics simulation, and the theoretical calculation of the structure of reactants were obtained in this paper. It also can be concluded by the results and discussion as follows:

- (1) The calculated results from density functional theory (DFT) indicated the average bond length in MoS<sub>2</sub> crystal, the order of Mulliken overlap population of Mo–S bond in MoS<sub>2</sub> slab, the electron density of (1 0 0) slab, (1 1 0) slab, (0 0 1) slab of MoS<sub>2</sub> and the electron density difference diagram, which confirmed that (0 0 1) cleavage surface was the weakest and easy to deposit during the thermal decomposition of MoS<sub>2</sub>.
- (2) The dynamics simulation and calculated results were in agreement with the experimental results of the thermal decomposition of  $MoS_2$ . Desulfuration reaction of thermal decomposition of  $MoS_2$  was carried out in two steps  $(MoS_2 \rightarrow Mo_2S_3 \rightarrow Mo)$ . The temperature of the reaction was higher than 1203 °C, above which in the first step  $MoS_2$  decomposed into  $Mo_2S_3$  which was not stable and would remove the three residual sulfur atoms in the following two steps. Two sulfur atoms were removed first and the other sulfur atom was then removed until molybdenum metal was produced.

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